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(54) METHOD FOR MANUFACTURING POLYMERIC COMPOUND FOR PHOTORESIST, AND RESIN COMPOSITION FOR PHOTORESIST

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a method for manufacturing a polymeric compound for a photoresist highly soluble in a resist solvent comprising a glycol-based solvent, an ester-based solvent, a ketone-based solvent or the like.

SOLUTION: The method for manufacturing a polymeric compound for a photoresist exhibiting changes in solubility in an alkali by an action of an acid comprises a step for polymerization using as a polymerization solvent one or more solvents selected among a glycol-based solvent, an ester-based solvent and a ketone-based solvent followed by a filtration treatment of the polymerization reaction liquid containing the resultant polymer. Preferably, the polymerization solvent is at least one selected among propylene glycol monomethyl ether, propylene glycol monomethyl ether acetate, ethyl lactate and methyl isobutyl ketone.

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CLAIMS

[Claim(s)]

[Claim 1] The manufacture approach of the high molecular compound for photoresists which is the manufacture approach of the high molecular compound for photoresists that the solubility over alkali changes with operations of an acid, carries out a polymerization using one sort or two sorts or more of solvents chosen from a glycol system solvent, ester solvent, and ketone solvent, and includes the process which carries out filtration processing of the polymerization reaction liquid containing the generated polymer as a polymerization solvent.

[Claim 2] The manufacture approach of the high molecular compound for photoresists according to claim 1 that glycol system solvents are a propylene glycol system solvent and/or an ethylene glycol system solvent.

[Claim 3] The manufacture approach of the high molecular compound for photoresists according to claim 1 that ester solvent is a lactate system solvent and/or propionic-acid ester solvent.

[Claim 4] The manufacture approach of the high molecular compound for photoresists according to claim 1 that polymerization solvents are at least one or more solvents chosen from propylene glycol monomethyl ether, propylene-glycol-monomethyl-ether acetate, ethyl lactate, and methyl isobutyl ketone.

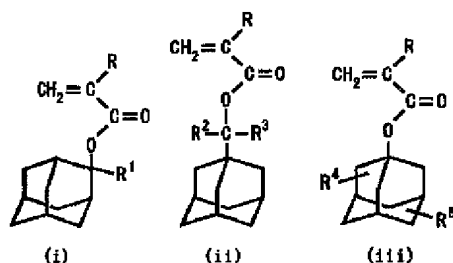
[Claim 5] The manufacture approach of the high molecular compound for photoresists according to claim 1 that a polymerization solvent is in any of a propylene-glycol-monomethyl-ether acetate independent solvent, the mixed solvent of propylene-glycol-monomethyl-ether acetate and propylene glycol monomethyl ether, or the mixed solvent of propylene-glycol-monomethyl-ether acetate and ethyl lactate.

[Claim 6] The manufacture approach of the high molecular compound for photoresists given in which term of claims 1-5 using a dropping polymerization method as a polymerization method.

[Claim 7] The manufacture approach of the high molecular compound for photoresists given in which term of claims 1-6 which are the acrylic polymers obtained by carrying out the polymerization of the monomer mixture with which said high molecular compound contains the monomer which has an alicyclic frame.

[Claim 8] Said high molecular compound is the following type (i) – (iii).

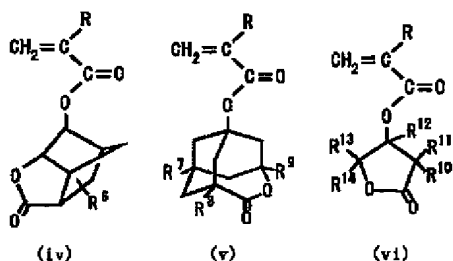
[Formula 1]



(R shows a hydrogen atom or a methyl group among a formula.) R^1 – R^3 show the alkyl group of carbon numbers 1–3 independently, respectively. R^4 and R^5 show a hydrogen atom, hydroxyl, an oxo-radical, or a carboxyl group independently, respectively. However, it is the manufacture approach of the high molecular compound for photoresists according to claim 7 which is the acrylic polymer obtained by carrying out the polymerization of the monomer mixture containing the monomer which has the alicyclic frame expressed with which formula chosen from at least one side being substituents other than a hydrogen atom among R^4 and R^5 .

[Claim 9] The manufacture approach of the high molecular compound for photoresists given in which term of claims 1–6 which are the acrylic polymers obtained by carrying out the polymerization of the monomer mixture with which said high molecular compound contains the monomer which has a lactone frame.

[Claim 10] said high molecular compound -- following type (iv) – (vi) -- [Formula 2]

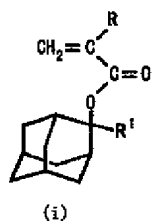


(R shows a hydrogen atom or a methyl group among a formula.) R^6 shows a hydrogen atom or the hydrocarbon group of carbon numbers 1–13. R^7 – R^{14} are the manufacture approach of the high molecular compound for photoresists according to claim 9 which is the acrylic polymer independently obtained by carrying out the polymerization of the monomer mixture containing the monomer which has the lactone frame expressed with which formula chosen from a hydrogen atom or a methyl group being shown, respectively.

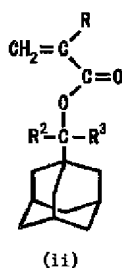
[Claim 11] The manufacture approach of the high molecular compound for photoresists given in which term of claims 1–10 which are the acrylic polymers obtained by said high molecular compound carrying out the polymerization of the monomer which has an alicyclic frame, and the monomer which has a lactone frame.

[Claim 12] Said high molecular compound is the following type (i).

[Formula 3]

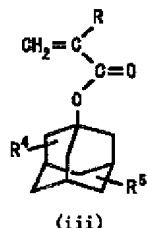


(R shows a hydrogen atom or a methyl group among a formula.) R1 -- the alkyl group of carbon numbers 1-3 -- being shown -- the monomer expressed and the following formula (ii) -- [Formula 4]

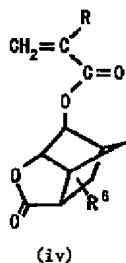


(R shows a hydrogen atom or a methyl group among a formula.) R2 and R3 -- respectively -- independent -- the alkyl group of carbon numbers 1-3 -- being shown -- at least a kind of monomer chosen from the monomer expressed, and the following formula (iii)

[Formula 5]



(R shows a hydrogen atom or a methyl group among a formula.) R4 and R5 show a hydrogen atom, hydroxyl, an oxo-radical, or a carboxyl group independently, respectively. however, the inside of R4 and R5 -- at least one side -- substituents other than a hydrogen atom -- it is -- the monomer expressed and the following formula (iv) -- [Formula 6]



(R shows a hydrogen atom or a methyl group among a formula.) R6 -- a hydrogen atom or the hydrocarbon group of carbon numbers 1-13 -- being shown -- the manufacture approach of the high molecular compound for photoresists according to claim 11 which is the acrylic polymer obtained by carrying out the polymerization of the monomer mixture which contains the monomer expressed at least.

[Claim 13] The resin constituent for photoresists which contains in which term of claims 1-12 at least the high molecular compound for photoresists obtained by the approach of a publication, and a photo-oxide generating agent.

[Claim 14] The resin constituent for photoresists according to claim 13 which contains as a solvent one sort or two sorts or more of solvents chosen from a glycol system solvent, ester solvent, and ketone solvent.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the manufacture approach of the high molecular compound for photoresists used in case micro processing of a semi-conductor etc. is performed, and the resin constituent for photoresists containing this high molecular compound.

[0002]

[Description of the Prior Art] The resin for resists used by the semi-conductor production process must have properties, such as adhesion to the property and silicon wafer from which the exposure section changes with optical exposures to alkali fusibility, plasma-etching resistance, and transparency over the light to be used. Although this resin for resists is used as a solution containing several sorts of additives for adjusting the polymer, the photo-oxide generating agent, and the above-mentioned property which are generally base resin, in order to prepare the resin for resists according to an application, it is very important for it that the polymer which is base resin is equipped with each above-mentioned property with sufficient balance.

[0003] In recent years, integration progresses, as for the semiconductor integrated circuit, LSI and VLSI are put in practical use, and with this, the minimum pattern reaches a submicron field and is in the inclination further made detailed. The activity of the lithography technique of covering with a resist a processed substrate [in which the thin film was formed] top in formation of a detailed pattern, developing negatives after performing selection exposure, and obtaining a resist pattern is indispensable. And as the exposure light source used for this, although ultraviolet rays were used, far ultraviolet rays with more short wavelength, an electron ray, an X-ray, etc. have come to be used as the light source with detailed-izing of a pattern at the beginning.

[0004] Therefore, corresponding to the lithography technique especially using an excimer laser (KrF laser with a wavelength of 248nm, ArF laser with a wavelength of 193nm), the resist ingredient which has high definition, high sensitivity, and the outstanding dry etching-proof nature is demanded. Although many things to which the conventional resist uses phenol resin or novolak resin as the base have been developed, although the aromatic series ring is included and being excelled in dry etching-proof nature, if these ingredients have low transparency and result in ArF laser to KrF laser wavelength, they are opaque. For this reason, if conventional resin was used, the pattern of detailed-izing was not able to be obtained.

[0005] Various kinds of proposals are made about the high sensitivity resist using an acid catalyst and the chemistry magnification effectiveness. The resist constituent which more specifically consists of

combination of the photo-oxide generating agent which generates an acid by the exposure of (1) activity beams of light (ultraviolet rays, far ultraviolet rays, vacuum-ultraviolet light, an electron ray, an X-ray, various laser light, etc.), and the polymer which has the alkali fusibility radical protected by the radical (protective group) from which it is easy to be desorbed with (2) acids attracts attention. A protective group reacts with the acid generated from the photo-oxide generating agent, the exposure field of the resist film serves as alkali fusibility, and a big change produces it in a solubility property with an unexposed field. If negatives are developed with an alkali water solution, an exposure field will be selectively removed by the developer used after that, and it will become a positive resist with it, and if negatives are developed with a non-polar solvent, in order that the solubility of an exposure field may decrease, it remains, and it becomes negative resist. thus, the thing for which this resist constituent chooses a developer -- a positive type and a negative mold -- it is available to any resist. Since the chemistry magnification effectiveness which promotes the elimination reaction (cleavage reaction) of a protective group by making into a catalyst the acid generated from a photo-oxide generating agent is shown, this resist constituent serves as a chemistry magnification mold in which high sensitivity is shown.

[0006] Recently, although the t-butyl methacrylate polymer is proposed as a transparent resist to excimer light, this resist lacks in dry etching-proof nature. The chemistry magnification mold resist which has the unit which has an alicyclic frame as what has dry etching-proof nature and has transparency to the wavelength of KrF laser and ArF laser further is reported (JP,4-39665,A, JP,5-257284,A, JP,5-265212,A, JP,7-234511,A, JP,9-73173,A, etc.). Furthermore, in order to raise the adhesion to a substrate, the resist which incorporated into the polymer the unit which has a lactone frame is also reported (JP,2000-26446,A, JP,2001-64325,A, JP,2001-109154,A, etc.).

[0007] On the other hand, as a solvent of these chemistry magnification mold resist, want of changeover to one sort or two sorts or more of solvents chosen from a glycol system solvent, ester solvent, and ketone solvent has been mounting from standpoints, such as handling nature and spreading engine performance. However, when the mothball of the polymer which was made to carry out a polymerization, using a tetrahydrofuran and dioxane as a polymerization solvent, and was refined and obtained by approaches, such as precipitate and reprecipitation, was carried out to which solvent of a glycol system solvent, ester solvent, or ketone solvent, it had the problem of a polymer depositing.

[0008]

[Problem(s) to be Solved by the Invention] Therefore, the object of this invention is to offer the resin constituent for photoresists which contains the manufacture approach of the soluble high high molecular compound for photoresists, and this high molecular compound to the solvent for resists which consists of one sort or two sorts or more of solvents chosen from a glycol system solvent, ester solvent, and ketone solvent.

[0009]

[Means for Solving the Problem] this invention persons found out that the high molecular compound for photoresists which melts into the solvent for resists certainly could be obtained easily by carrying out a polymerization using one sort or two sorts or more of solvents chosen from a glycol system solvent, ester solvent, and ketone solvent, and carrying out filtration processing after a polymerization reaction, as a result of inquiring wholeheartedly, in order to attain the above-mentioned object.

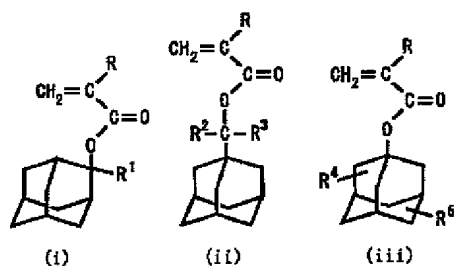
[0010] That is, this invention is the manufacture approach of the high molecular compound for photoresists that the solubility over alkali changes with operations of an acid, and offers the manufacture approach of the high molecular compound for photoresists including the process which carries out filtration processing of the polymerization reaction liquid which carries out a polymerization as a polymerization solvent using one sort or two sorts or more of solvents chosen from a glycol system solvent, ester solvent, and ketone solvent, and contains the generated polymer. Glycol system solvents may be a propylene glycol system solvent and/or an ethylene glycol system solvent, and ester solvent may be a lactate system solvent and/or propionic-acid ester solvent.

[0011] It is desirable that they are at least one or more solvents chosen from propylene glycol monomethyl ether, propylene-glycol-monomethyl-ether acetate, ethyl lactate, and methyl isobutyl ketone as a polymerization solvent in the above-mentioned approach, and which solvent of a propylene-glycol-monomethyl-ether acetate independent solvent, the mixed solvent of propylene-glycol-monomethyl-ether acetate and propylene glycol monomethyl ether, or the mixed solvent of propylene-glycol-monomethyl-ether acetate and ethyl lactate is desirable especially.

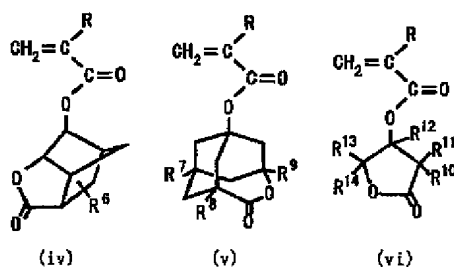
[0012] In the manufacture approach of the high molecular compound for photoresists of this invention, a dropping polymerization method may be used as a polymerization method. It is desirable that it is in any of the acrylic polymer obtained by said high molecular compound carrying out the polymerization of the monomer which has (A) alicyclic frame, and the other monomers, the acrylic polymer obtained by carrying out the polymerization of the monomer component of the monomer and others which have (B) lactone frame, and the acrylic polymer obtained by carrying out the polymerization of the monomer which has (C) alicyclic frame, and the monomer which has a lactone frame.

[0013] As a monomer which has said alicyclic frame, they are the following type (i) - (iii).

[Formula 7]



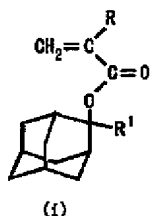
(R shows a hydrogen atom or a methyl group among a formula.) R¹-R³ show the alkyl group of carbon numbers 1-3 independently, respectively. R⁴ and R⁵ show a hydrogen atom, hydroxyl, an oxo-radical, or a carboxyl group independently, respectively. However, at least one side has the desirable monomer which has the alicyclic frame expressed with which formula chosen from being substituents other than a hydrogen atom among R⁴ and R⁵. moreover -- as the monomer which has said lactone frame -- following type (iv) - (vi) -- [Formula 8]



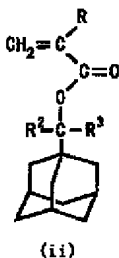
(R shows a hydrogen atom or a methyl group among a formula.) R6 shows a hydrogen atom or the hydrocarbon group of carbon numbers 1–13. R7–R14 have respectively the monomer more desirable than which formula chosen from a hydrogen atom or a methyl group being shown which has the lactone frame by which a table is carried out independently.

[0014] Especially, said high molecular compound is the following type (i).

[Formula 9]

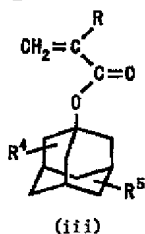


(R shows a hydrogen atom or a methyl group among a formula.) R1 — the alkyl group of carbon numbers 1–3 — being shown — the monomer expressed and the following formula (ii) — [Formula 10]



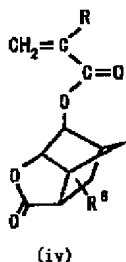
(R shows a hydrogen atom or a methyl group among a formula.) R2 and R3 — respectively — independent — the alkyl group of carbon numbers 1–3 — being shown — at least a kind of monomer chosen from the monomer expressed, and the following formula (iii)

[Formula 11]



(R shows a hydrogen atom or a methyl group among a formula.) R4 and R5 show a hydrogen atom, hydroxyl, an oxo-radical, or a carboxyl group independently, respectively. however, the inside of R4 and R5 — at least

one side -- substituents other than a hydrogen atom -- it is -- the monomer expressed and the following formula (iv) -- [Formula 12]



(R shows a hydrogen atom or a methyl group among a formula.) R6 -- a hydrogen atom or the hydrocarbon group of carbon numbers 1-13 -- being shown -- the acrylic polymer obtained by carrying out the polymerization of the monomer mixture which contains the monomer expressed at least is desirable.

[0015] Furthermore, this invention offers the resin constituent for photoresists which contains at least the high molecular compound for photoresists obtained by the above-mentioned approach, and a photo-oxide generating agent. This resin constituent for photoresists may also contain one sort or two sorts or more of solvents chosen from a glycol system solvent, ester solvent, and ketone solvent as a solvent.

[0016] In addition, on these descriptions, it may name generically "an acrylic (meta)", "acryloyl", and "methacryloyl one" "acryloyl (meta) etc." for an "acrylic" and "methacrylic one."

[0017]

[Embodiment of the Invention] This invention is applicable to manufacture of the extensive high molecular compound for photoresists from which the solubility over alkali changes with operations of an acid.

[0018] The high molecular compound which has the alkali fusibility radical protected by the protective group (acid desorption nature protective group) from which it is easy to be desorbed with an acid is contained in the high molecular compound from which the solubility over alkali changes with operations of an acid. A carboxyl group, a sulfonyl group, etc. are mentioned as said alkali fusibility radical. As said acid desorption nature protective group, it is said carboxyl group etc. and the radical which forms ester, and the radical which has a tertiary carbon atom in a binding site with the oxygen atom of this ester is mentioned, for example. The alkali fusibility radical protected by the acid desorption nature protective group can be introduced into a polymer by using as a monomer the acrylic acid (meta) from which the carboxyl group was protected by the acid desorption nature protective group.

[0019] The high molecular compound for photoresists with which the manufacture approach of this invention is applied The acrylic polymer obtained by carrying out the polymerization of the monomer mixture containing the monomer which has (A) alicyclic frame especially, (B) The acrylic polymer obtained by carrying out the polymerization of the monomer mixture containing the monomer which has a lactone frame, Or it is desirable that it is the acrylic polymer obtained by carrying out the polymerization of the monomer which has (C) alicyclic frame, and the monomer which has a lactone frame, and the acrylic polymer obtained especially by carrying out the polymerization of the monomer which has (C) alicyclic frame, and the monomer which has a lactone frame is the most desirable.

[0020] The monomer which has said alicyclic frame can give transparency and dry etching resistance to the high molecular compound obtained by carrying out a polymerization, and its resin constituent. Moreover, the

thing containing the protective group (the alicyclic radical may be a direct protective group) from which it is desorbed especially with an acid can give high sensibility in resist utilization. Moreover, the monomer which has an alicyclic frame can give the effectiveness which raises the adhesion to a substrate by having substituents, such as hydroxyl, an oxo-radical, and a carboxyl group, to a ring.

[0021] As a monomer which has an alicyclic frame, the acrylic ester which contains an alicyclic frame in the alcoholic section of ester (meta) is desirable. As a desirable alicyclic frame, an adamantane frame, an isobornane frame, a cyclohexane frame, a tricyclodecane frame, etc. are mentioned, for example. Said alicyclic frame may have substituents, such as an alkyl group, a carboxyl group, and hydroxyl. The acrylic ester which has the adamantane frame expressed with said formula (i) – (iii) especially (meta) is used preferably. These monomers are independent, or they can be used, combining them two or more sorts.

[0022] As a compound expressed with a formula (i), 2-(meth)acryloyloxy-2-methyl adamantane ($R_1=CH_3$), 2-(meth)acryloyloxy-2-ethyl adamantane ($R_1=C_2H_5$), etc. are mentioned, for example.

[0023] As a typical compound expressed with a formula (ii) For example,

1-(1-(meth)acryloyloxy-1-methylethyl) adamantane ($R_2=CH_3$, $R_3=CH_3$),
1-(1-(meth)acryloyloxy-1-methylpropyl) adamantane ($R_2=CH_3$, $R_3=C_2H_5$), 1-(1-(meth)acryloyloxy-1-ethylpropyl) adamantane ($R_2=C_2H_5$, $R_3=C_2H_5$), 1-(1-(meth)acryloyloxy-1-methylbutyl) adamantane ($R_2=CH_3$, $R_3=C_3H_7$), etc. are mentioned.

[0024] As a typical example of a compound expressed with a formula (iii) 1-(meth)acryloyloxy-3-hydroxy adamantane (it $OH(s)$ $R_4=$ —) $R_5=H$, 1-(meth)acryloyloxy-3, 5-dihydroxy adamantane ($R_4=R_5=OH$), 1-(meth)acryloyloxy adamantane-4-ON (an $R_4=4$ -oxo-radical —) $R_5=H$, 1-(meth)acryloyloxy-3-carboxy adamantane ($R_4=H$, $R_5=COOH$), 1-(meth)acryloyloxy-3, 5-dicarboxy adamantane ($R_4=R_5=COOH$), etc. are mentioned.

[0025] Moreover, the monomer which has said lactone frame gives the adhesion over a substrate to the high molecular compound obtained by carrying out a polymerization, and its resin constituent. Moreover, the thing containing the protective group (the lactone radical may be a direct protective group) from which it is desorbed especially with an acid can give high sensibility in resist utilization.

[0026] As a monomer which has a lactone frame, the acrylic ester which contains a lactone frame in the alcoholic section of ester (meta) is desirable. For example, what is chosen from the group which consists of the acrylate which has a gamma-butyrolactone ring (meta), the acrylate which has delta-valerolactone ring (meta), acrylate which has epsilon-caprolactone ring (meta), and a derivative which has substituents, such as an alkyl group, a carbonyl group, and hydroxyl, on the lactone ring of these monomers is desirable. The acrylate which has the lactone frame expressed with said formula (iv) – (vi) especially (meta) is used preferably. These monomers are independent, or they can be used, combining them two or more sorts.

[0027] As a typical example of a compound expressed with a formula (iv), 5-(meth)acryloyloxy-3-oxatricyclo [4.2.1.0^{4,8}] nonane-2-ON [=5-(meth)acryloyloxy-2, and 6-norbornane KARUBO lactone] ($R_6=H$) etc. is mentioned.

[0028] as the typical example of a compound expressed with a formula (v) —

1-(meth)acryloyloxy-4-oxatricyclo [— 4. — 3.1.13, 8] undecane-5-ON ($R_7=R_8=R_9=H$), etc. are mentioned.

[0029] As a typical example of a compound expressed with a formula (vi),

beta-(meth)acryloyloxy-gamma-butyrolactone ($R_{10}=R_{11}=R_{12}=R_{13}=R_{14}=H$),

beta-(meth)acryloyloxy-beta-methyl-gamma-butyrolactone ($R_{10}=R_{11}=H$, $R_{12}=CH_3$, $R_{13}=R_{14}=H$), etc. are mentioned.

[0030] The acrylic polymer obtained by carrying out the polymerization of the monomer mixture which contains at least a kind of monomer chosen from the monomer expressed with the monomer and formula (ii) which are expressed with a formula (i) especially as a high molecular compound for photoresists with which the manufacture approach of this invention is applied, the monomer expressed with a formula (iii), and the monomer expressed with a formula (iv) is desirable.

[0031] Especially In the 2-(meth)acryloyloxy-2-methyl adamantane and the formula (ii) which are $R_1=CH_3$ in a formula (i) At least a kind of monomer chosen from 1-(1-(meth)acryloyloxy-1-methylethyl) adamantane which are $R_2=CH_3$ and $R_3=CH_3$, The 1-(meth)acryloyloxy-3-hydroxy adamantane which are $R_4=3-OH$ and $R_5=H$ in a formula (iii), In a formula (iv) The polymerization of the monomer mixture which contains at least the 5-(meth)acryloyloxy-3-oxatricyclo [4.2.1.0^{4,8}] nonane-2-ON [=5-(meth)acryloyloxy -2, and 6-norbornane KARUBO lactone] which is $R_6=H$ is carried out. The acrylic polymer obtained is desirable.

[0032] In said polymer, as a ratio of the monomer which constitutes a polymer The unit corresponding to a kind of monomer chosen from the formula (i) and the formula (ii) at least 22 – 58-mol % (preferably 25–55-mol %), It is desirable that the unit corresponding to 15–45-mol % (preferably 18–42-mol %) and a type (iv) in the unit corresponding to a formula (iii) is 15 – 45-mol % (preferably 18–42-mol %).

[0033] They are in a point including the process which carries out filtration processing of the polymerization reaction liquid containing the generated polymer while one sort or two sorts or more of solvents chosen from a glycol system solvent, ester solvent, and ketone solvent as a polymerization solvent are used for the main descriptions of this invention.

[0034] Ethylene glycol system solvents, such as propylene glycol system solvent; ethylene glycol monomethyl ether, such as propylene glycol monomethyl ether and propylene-glycol-monomethyl-ether acetate, ethylene glycol monomethyl ether acetate, ethylene glycol monoethyl ether, ethylene glycol monoethyl ether acetate, ethylene glycol monobutyl ether, and ethylene-glycol-monobutyl-ether acetate, etc. are contained in a glycol system solvent. Acetic-ester system solvents, such as propionic-acid ester solvent; methyl acetate, such as lactate system solvent; 3-methoxy methyl propionates, such as ethyl lactate, ethyl acetate, propyl acetate, and butyl acetate, etc. are contained in ester solvent. An acetone, a methyl ethyl ketone, methyl isobutyl ketone, a cyclohexanone, etc. are contained in ketone solvent.

[0035] The solvent which contains also in the above at least one sort or two sorts or more of compounds chosen from propylene glycol monomethyl ether, propylene-glycol-monomethyl-ether acetate, ethyl lactate, and methyl isobutyl ketone, for example is used preferably. Especially, in this invention, a propylene-glycol-monomethyl-ether acetate independent solvent, the mixed solvent of propylene-glycol-monomethyl-ether acetate and propylene glycol monomethyl ether, the mixed solvent of propylene-glycol-monomethyl-ether acetate and ethyl lactate, etc. are used preferably.

[0036] A polymerization can be performed by the solution polymerization method and the operation information of the common use generally performed by the solution polymerization method etc. can be used. As an approach of manufacturing the high molecular compound for photoresists of this invention especially, a dropping polymerization method is suitable. The monomer solution which dissolved in the organic solvent beforehand, and the polymerization initiator which dissolved in the organic solvent are prepared, respectively,

and, specifically, a dropping polymerization method is performed by approaches, such as the approach of trickling the mixed solution made to dissolve the approach of trickling said monomer solution and polymerization initiator solution respectively into the organic solvent held to constant temperature, (i) (ii) monomer, and a polymerization initiator in an organic solvent into the organic solvent held to constant temperature. By using a dropping polymerization method, a high molecular compound with the uniform copolymerization presentation acquired in the early stages of a polymerization and an anaphase can be obtained. Moreover, a polymerization initiator well-known as a polymerization initiator can be used.

[0037] Polymerization temperature is about 60–120 degrees C, and 40–150 degrees C of polymerization time amount are about 3 – 15 hours preferably for 1 to 24 hours, for example.

[0038] As for the barrier filter used for said filtration down stream processing, 0.01–3.0 microns of about 0.05–1.0-micron things are preferably used for an aperture. [0039] Although the solid-state which condenses the filtrate obtained by filtration down stream processing or filtrate, and is obtained may be used for preparation of the resin constituent for photoresists as it is, preparation of the resin constituent for photoresists may be presented with the solid-state which was made to fully dry the generated polymer after purification by approaches, such as precipitate and reprecipitation, and was obtained.

[0040] as the organic solvent used as said precipitate or a reprecipitation solvent -- for example, aliphatic hydrocarbon (a pentane --) alicyclic hydrocarbon (a cyclohexane --), such as a hexane, a heptane, and an octane aromatic hydrocarbon (benzene and toluene --), such as a methylcyclohexane a xylene etc. -- etc. -- hydrocarbon; -- halogenated aliphatic hydrocarbon (a methylene chloride --) halogenated-aromatics hydrocarbons (a chlorobenzene --), such as chloroform and a carbon tetrachloride a dichlorobenzene etc. -- etc. -- halogenated hydrocarbon; -- nitromethane -- nitro compound [, such as nitroethane,]; -- the nitril; chain-like ether (diethylether --), such as an acetonitrile and a benzonitrile cyclic ether (a tetrahydrofuran --), such as diisopropyl ether and dimethoxyethane dioxane etc. -- etc. -- ether; -- an acetone and a methyl ethyl ketone -- Ketones, such as methyl isobutyl ketone and diisobutyl ketone; Ethyl acetate, Ester, such as butyl acetate; Dimethyl carbonate, diethyl carbonate, Carboxylic acids [, such as alcoholic; acetic acid], such as carbonate; methanols, such as ethylene carbonate and propylene carbonate, ethanol, propanol, isopropanol, and a butanol; the mixed solvent containing water; and these solvents etc. is mentioned.

[0041] Especially, the mixed solvent which contains a hydrocarbon (especially aliphatic hydrocarbon, such as a hexane) at least is desirable as an organic solvent used as said precipitate or a reprecipitation solvent. such a solvent that contains a hydrocarbon at least -- setting -- the mixing ratio of a hydrocarbon and other solvents -- as a rate -- solvent = 10 / 90 – 99 / 1 of for example, hydrocarbon/and others (the volume ratio in 25 degrees C, and the following -- the same) -- desirable -- 30 / 70 – 98 / 2 -- it is about 50 / 50 to 97 / 3 still more preferably.

[0042] In this way, since the solubility over which solvents or these mixed solvents of the glycol system solvent suitably used as a solvent for resists, ester solvent, or ketone solvent is high, the high molecular compound obtained can be preferably used as a resin constituent for photoresists.

[0043] this invention -- the weight average molecular weight (Mw) of a high molecular compound -- 5,000–70,000 -- desirable -- 6,000 to about 40,000 -- it is -- degree of dispersion (Mw/Mn) -- for example, the polymer which is or less 2.5 (1.5–2.0) extent preferably is obtained 3.0 (1.0–3.0) or less. In addition,

weight average molecular weight (M_w) and number average molecular weight (M_n) show the standard polystyrene reduced property calculated by GPC measurement using a tetrahydrofuran solvent using a refractive-index meter (RI). Degree of dispersion (M_w/M_n) is computable from said measured value. Weight average molecular weight and degree of dispersion can be controlled by choosing suitably the class of initiator, the amount of an initiator and the monomer used, reaction temperature, etc. When weight average molecular weight and a degree of dispersion are too large, the resin for resists becomes cloudy or there is an inclination for resist properties, such as sensibility and resolution, to fall.

[0044] The resin constituent for photoresists of this invention contains at least the high molecular compound for photoresists and photo-oxide generating agent which were obtained by the approach of this invention.

[0045] The common use which generates an acid efficiently by exposure as a photo-oxide generating agent thru/or a well-known compound, For example, diazonium salt, iodonium salt (for example, diphenyl iodine hexafluorophosphate etc.), sulfonium salt (for example, triphenylsulfonium hexafluoroantimonate —) sulfonates [, such as triphenylsulfonium hexafluorophosphate and triphenyl sulfonium methanesulfonate,] [-- for example 1-phenyl-1-(4-methylphenyl) sulfonyloxy-1-benzoyl methane, 1, 2, 3-tris RUHONIRU oxymethyl benzene, 1, 3-dinitro-2-(4-phenyl sulfonyl oxymethyl) benzene,], such as 1-phenyl-1-(4-methylphenyl sulfonyl oxymethyl)-1-hydroxy-1-benzoyl methane, An OKISA thiazole derivative, s-triazine derivative, disulfon derivatives (diphenyl disulfon etc.), an imide compound, oxime sulfonate, a diazo naphthoquinone, benzoin tosylate, etc. can be used. These photo-oxide generating agents are independent, or they can be used, combining them two or more sorts.

[0046] the reinforcement of the acid which generates the amount of the photo-oxide generating agent used by optical exposure, the ratio of each monomeric unit in said high molecular compound, etc. -- responding -- suitably -- it can choose -- for example, said high-molecular-compound 100 weight section -- receiving -- 0.1 - 30 weight section -- desirable -- 1 - 25 weight section -- it can choose from the range of 2 - 20 weight section extent still more preferably.

[0047] Moreover, although it is chosen as arbitration according to the object, it is desirable [a solvent] to choose in consideration of the other reason, for example, the homogeneity of a paint film, an appearance, or safety at the same time the solvent used takes into consideration the solubility of a copolymer and a photo-oxide generating agent. As a solvent which has such a property, the glycol system solvent illustrated as the above-mentioned polymerization solvent, ester solvent, ketone solvent, and these mixed solvents can be mentioned, and it is suitably used as a solvent for resists, for example.

[0048] As a desirable solvent, propylene glycol monomethyl ether, propylene-glycol-monomethyl-ether acetate, ethyl lactate, and methyl isobutyl ketone are mentioned, and independent or two sorts or more are mixed, and it is used especially, for example. Especially, a propylene-glycol-monomethyl-ether acetate independent solvent, the mixed solvent of propylene-glycol-monomethyl-ether acetate and propylene glycol monomethyl ether, the mixed solvent of propylene-glycol-monomethyl-ether acetate and ethyl lactate, etc. are used preferably.

[0049] The resin constituent for photoresists may contain alkali meltable components, such as alkali fusibility resin (for example, novolak resin, phenol resin, imide resin, carboxyl group content resin, etc.), coloring agents (for example, color etc.), organic solvents (for example, hydrocarbons, halogenated

hydrocarbon, alcohols, ester, amides, ketones, ether, cellosolves, carbitols, glycol ether ester, these mixed solvents, etc.), etc.

[0050] This resin constituent for photoresists is applied on a base material or a substrate, and after drying, a detailed pattern can be formed in a high precision through a predetermined mask by exposing a beam of light to a paint film (resist film), forming a latent-image (or further BEKU after exposure deed) pattern, and subsequently developing it.

[0051] As a base material or a substrate, a silicon wafer, a metal, plastics, glass, a ceramic, etc. are mentioned. Spreading of the resin constituent for photoresists can be performed using the spreading means of common use, such as a spin coater, a dip coater, and a roller coater. 0.1–20 micrometers of thickness of a paint film are about 0.3–2 micrometers preferably, for example.

[0052] The beam of light of various wavelength, for example, ultraviolet rays, an X-ray, etc. can be used for exposure, and g line, i line, excimer lasers (for example, XeCl, KrF, KrCl, ArF, ArCl, etc.), etc. are usually used for it by the object for semi-conductor resists. exposure energy — for example, 1 – 1000 mJ/cm² — it is about two 10 – 500 mJ/cm preferably.

[0053] An acid generates from a photo-oxide generating agent by optical exposure, with this acid, protective groups (desorption nature machine), such as a carboxyl group of the alkali fusibility unit of said high molecular compound, **** promptly, and the carboxyl group which contributes to solubilization generates, for example. Therefore, a predetermined pattern can be formed with a sufficient precision by development by water or the alkali developer.

[0054]

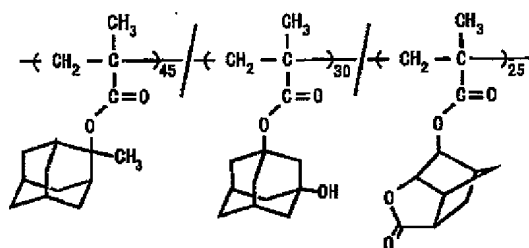
[Effect of the Invention] Since filtration processing of the polymerization reaction liquid is carried out according to this invention, using one sort or two sorts or more of solvents chosen from a glycol system solvent, ester solvent, and ketone solvent as a polymerization solvent, the high molecular compound for photoresists in which high solubility is shown to one sort or two sorts of solvents chosen from the glycol system solvent used widely as a solvent for resists, ester solvent, and ketone solvent can be manufactured simply. Moreover, the high molecular compound for photoresists which has moderate weight average molecular weight (M_w) and a small degree of dispersion (M_w/M_n) can be manufactured. Furthermore, the high molecular compound for photoresists in which high dry etching resistance, substrate adhesion, and alkali fusibility are shown can be manufactured.

[0055]

[Example] This invention is not limited by these examples although this invention is explained more below at a detail based on an example. The figure at the lower right of the parenthesis in a structure expression shows mol % of the preparation monomer corresponding to this monomeric unit. The physical properties of the obtained polymer were measured as follows. The main polymerization conditions are shown in a table 1.

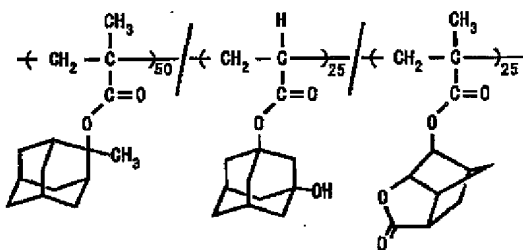
[0056] [Weight-average-molecular-weight (M_w) and degree-of-dispersion (M_w/M_n)] weight average molecular weight (M_w) and number average molecular weight (M_n) show the standard polystyrene reduced property calculated by GPC measurement using a tetrahydrofuran solvent using a refractive-index meter (RI). GPC used what connected Showa Denko column KF-806L with 3 serials, and performed it the condition for column temperature [of 40 degrees C], RI temperature [of 40 degrees C], and 0.8ml/of the tetrahydrofuran rates of flow. Degree of dispersion (M_w/M_n) was computed from said measured value.

[0057] Composition of the resin of the example 1 following structure [** 13]



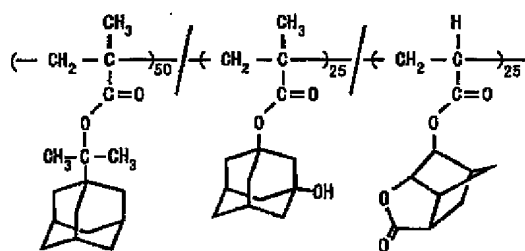
Put propylene-glycol-monomethyl-ether acetate (PGMEA) 32g into the round bottom flask equipped with reflux tubing, the stirring child, and the method cock of three under nitrogen-gas-atmosphere mind, keep temperature at 100 degrees C, and, stirring (A) 2-methacryloyloxy-2-methyl adamantane (2MMA) 36.37g, (B) 1-methacryloyloxy-3-hydroxy adamantane (HMA) 24.46g, (C) — 5-methacryloyloxy-2 and 6-norbornane KARUBO lactone (MNBL) 19.17g (a monomer presentation ratio — (A):(B):(C) =45:30:25 (the mole ratio at the time of preparation —)) The monomer solution which mixed dimethyl-2,2'-azobisisobutyrate (initiator; product V-601 made from Wako Pure Chem industry) 3.2g and PGMEA288g was dropped with constant speed over 6 hours like the following. After filtering the obtained reaction mixture (polymerization dope) with the filter of 0.1 microns of apertures after polymerization reaction termination, it was dropped stirring in the 9:1 (volume ratio; 25 degrees C) mixed liquor of the hexane of the amount of about 10 times of this reaction mixture, and ethyl acetate, and refined by carrying out produced precipitate a ** exception. 56g of desired resin was obtained by dissolving the collected precipitate in PGMEA320g again after reduced pressure drying, and repeating the precipitate purification actuation using an above-mentioned hexane and the mixed solvent of ethyl acetate. When GPC analysis of the collected polymer was carried out, Mw (weight average molecular weight) was 6800, and degree of dispersion (Mw/Mn) was 2.10.

[0058] Composition of the resin of the example 2 following structure [** 14]



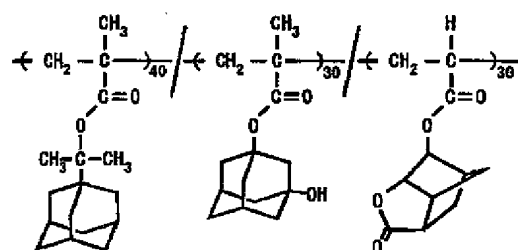
In an example 1 as a monomer component (A)2-methacryloyloxy-2-methyl adamantane (2MMA) 41.05g, (B) 1-acryloyloxy-3-hydroxy adamantane (HAA) 19.47g, (C) — except having used 5-methacryloyloxy-2 and 6-norbornane KARUBO lactone (MNBL) 19.47g (a monomer presentation ratio — (A):(B):(C) =50:25:25), when reacted by the same actuation as an example 1, 60g of desired resin was obtained. When GPC analysis of the collected polymer was carried out, Mw (weight average molecular weight) was 13400, and degree of dispersion (Mw/Mn) was 2.4.

[0059] Composition of the resin of the example 3 following structure [** 15]



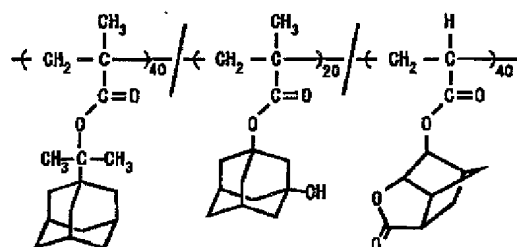
In an example 1 as a monomer component (A)1-(1-methacryloyloxy-1-methylethyl) adamantane (IAM) 43.31g, (B) 1-methacryloyloxy-3-hydroxy adamantane (HMA) 19.50g, (C) -- 5-acryloyloxy -2 and 6-norbornane KARUBO lactone (ANBL) 17.19g (a monomer presentation ratio -- (A):(B):(C) =50:25:25) -- Except having used 2.0g of initiators, when reacted by the same actuation as an example 1, 63g of desired resin was obtained. When GPC analysis of the collected polymer was carried out, Mw (weight average molecular weight) was 11400, and degree of dispersion (Mw/Mn) was 1.91.

[0060] Composition of the resin of the example 4 following structure [** 16]



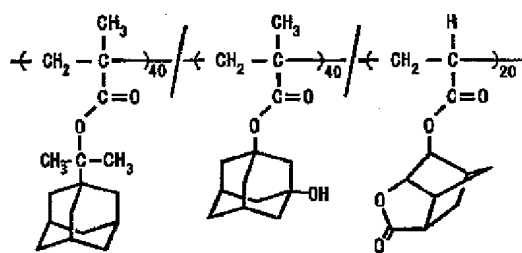
in the example 3, except having used (A)35.23g, (B)23.80g, and (C)20.97g (a monomer presentation ratio -- (A):(B):(C) =40:30:30) as a monomer component, when reacted by the same actuation as an example 3, 58g of desired resin was obtained. When GPC analysis of the collected polymer was carried out, Mw (weight average molecular weight) was 8300, and degree of dispersion (Mw/Mn) was 2.03.

[0061] Composition of the resin of the example 5 following structure [** 17]



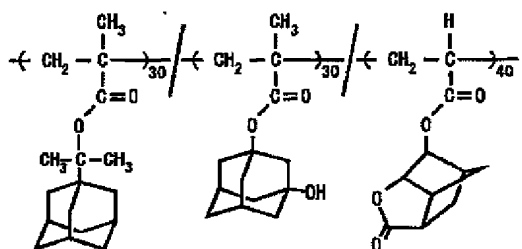
in the example 3, except having used (A)35.65g, (B)16.05g, and (C)28.30g (a monomer presentation ratio -- (A):(B):(C) =40:20:40) as a monomer component, when reacted by the same actuation as an example 3, 59g of desired resin was obtained. When GPC analysis of the collected polymer was carried out, Mw (weight average molecular weight) was 8600, and degree of dispersion (Mw/Mn) was 2.10.

[0062] Composition of the resin of the example 6 following structure [** 18]



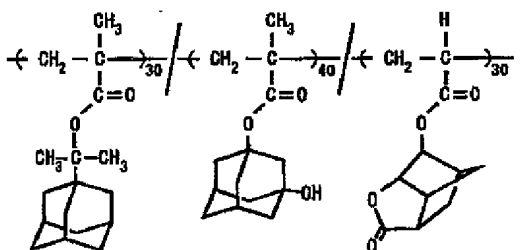
in the example 3, except having used (A)34.82g, (B)31.36g, and (C)13.82g (a monomer presentation ratio — (A):(B):(C) = 40:40:20) as a monomer component, when reacted by the same actuation as an example 3, 58g of desired resin was obtained. When GPC analysis of the collected polymer was carried out, Mw (weight average molecular weight) was 9100, and degree of dispersion (Mw/Mn) was 2.15.

[0063] Composition of the resin of the example 7 following structure [** 19]



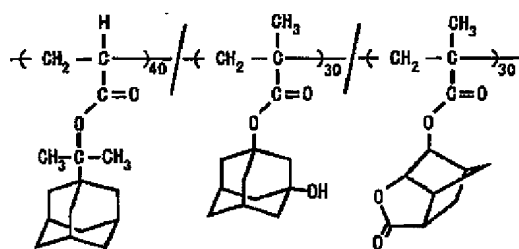
in the example 3, except having used (A)27.03g, (B)24.35g, and (C)28.62g (a monomer presentation ratio — (A):(B):(C) = 30:30:40) as a monomer component, when reacted by the same actuation as an example 3, 60g of desired resin was obtained. When GPC analysis of the collected polymer was carried out, Mw (weight average molecular weight) was 15100, and degree of dispersion (Mw/Mn) was 3.70.

[0064] Composition of the resin of the example 8 following structure [** 20]



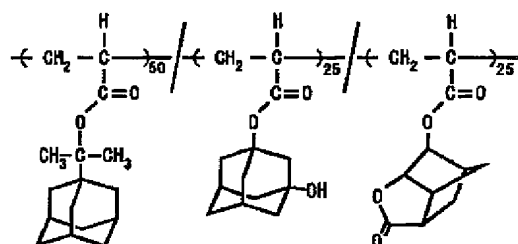
in the example 3, except having used (A)26.71g, (B)32.08g, and (C)21.21g (a monomer presentation ratio — (A):(B):(C) = 30:40:30) as a monomer component, when reacted by the same actuation as an example 3, 62g of desired resin was obtained. When GPC analysis of the collected polymer was carried out, Mw (weight average molecular weight) was 14400, and degree of dispersion (Mw/Mn) was 2.03.

[0065] Composition of the resin of the example 9 following structure [** 21]



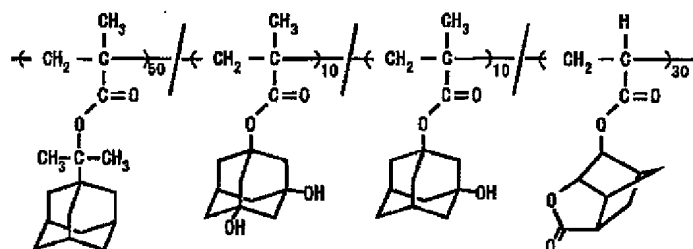
In an example 3 as a monomer component (A)1-(1-acryloyloxy-1-methylethyl) adamantane (IAA) 33.54g, (B) 1-methacryloyloxy-3-hydroxy adamantane (HMA) 23.94g, (C) — except having used 5-methacryloyloxy-2 and 6-norbornane KARUBO lactone (MNBL) 22.52g (a monomer presentation ratio — (A):(B):(C) =40:30:30), when reacted by the same actuation as an example 3, 58g of desired resin was obtained. When GPC analysis of the collected polymer was carried out, Mw (weight average molecular weight) was 6800, and degree of dispersion (Mw/Mn) was 1.94.

[0066] Composition of the resin of the example 10 following structure [** 22]



In an example 3 as a monomer component (A)1-(1-acryloyloxy-1-methylethyl) adamantane (IAA) 42.85g, (B) 1-acryloyloxy-3-hydroxy adamantane (HAA) 19.18g, (C) — except having used 5-acryloyloxy-2 and 6-norbornane KARUBO lactone (ANBL) 17.97g (a monomer presentation ratio — (A):(B):(C) =50:25:25), when reacted by the same actuation as an example 3, 54g of desired resin was obtained. When GPC analysis of the collected polymer was carried out, Mw (weight average molecular weight) was 7000, and degree of dispersion (Mw/Mn) was 2.11.

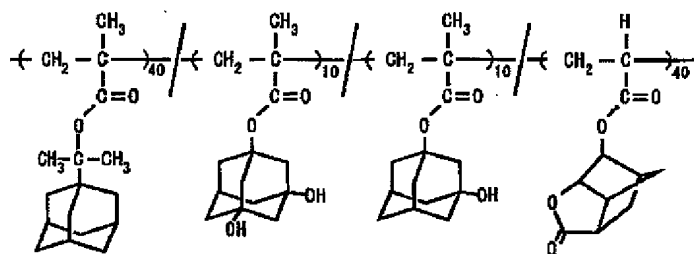
[0067] Composition of the resin of the example 11 following structure [** 23]



In an example 1 as a monomer component (A)1-(1-methacryloyloxy-1-methylethyl) adamantane (IAM) 43.27g, (B) 1-methacryloyloxy-3,5-dihydroxyadamantane (DHMA) 8.32g, (C) 1-methacryloyloxy-3-hydroxyadamantane (HMA) 7.80g, (D) — 5-acryloyloxy-2 and 6-norbornane KARUBO lactone (ANBL) 20.61g (a monomer presentation ratio — (A):(B):(C):(D) =50:10:10:30) — Except having made temperature into 75 degrees C using 8.0g of initiators, when reacted by the same actuation as

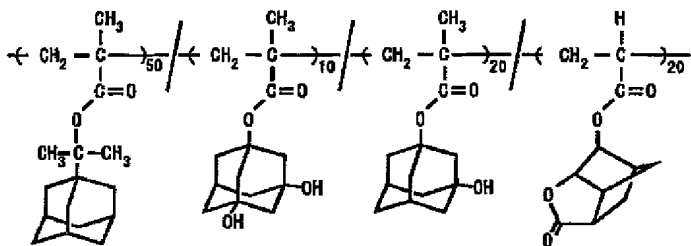
an example 1, 69g of desired resin was obtained. When GPC analysis of the collected polymer was carried out, Mw (weight average molecular weight) was 14900, and degree of dispersion (Mw/Mn) was 3.17.

[0068] Composition of the resin of the example 12 following structure [** 24]



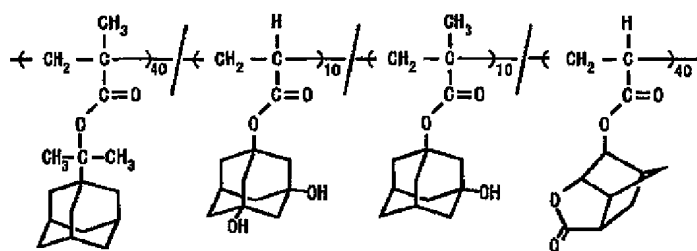
in the example 11, except having used (A)35.41g, (B)8.51g, (C)7.97g, and (D)28.11g (a monomer presentation ratio -- (A):(B):(C):(D) =40:10:10:40) as a monomer component, when reacted by the same actuation as an example 11, 72g of desired resin was obtained. When GPC analysis of the collected polymer was carried out, Mw (weight average molecular weight) was 13200, and degree of dispersion (Mw/Mn) was 2.98.

[0069] Composition of the resin of the example 13 following structure [** 25]



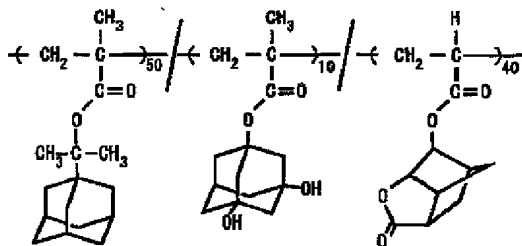
Put the bottom of nitrogen-gas-atmosphere mind, PGMEA26g, and propylene-glycol-monomethyl-ether (PGME) 6g into the round bottom flask equipped with reflux tubing, the stirring child, and the method cock of three, keep temperature at 75 degrees C, and, stirring (A) 1-(1-methacryloyloxy-1-methylethyl) adamantane (IAM) 42.78g, (B) 1-methacryloyloxy - 3 and 5-dihydroxy adamantane (DHMA) 8.23g, (C) 1-methacryloyloxy-3-hydroxy adamantane (HMA) 15.41g, (D) -- 5-acryloyloxy -2 and 6-norbornane KARUBO lactone (ANBL) 13.58g (a monomer presentation ratio -- (A):(B):(C):(D) =50:10:20:20) -- And the monomer solution which mixed dimethyl-2,2'-azobisisobutyrate (initiator; product V-601 made from Wako Pure Chem industry) 8.0g, PGMEA230g, and PGME58g was dropped with constant speed over 6 hours. After filtering the obtained reaction mixture (polymerization dope) with the filter of 0.1 microns of apertures after polymerization reaction termination, it was dropped stirring in the 9:1 (volume ratio; 25 degrees C) mixed liquor of the hexane of the amount of about 10 times of this reaction mixture, and ethyl acetate, and refined by carrying out produced precipitate a ** exception. 65g of desired resin was obtained by dissolving the collected precipitate in the mixed solvent (weight ratio 8:2) of PGMEA256g and PGME64g again after reduced pressure drying, and repeating the precipitate purification actuation using an above-mentioned hexane and the mixed solvent of ethyl acetate. When GPC analysis of the collected polymer was carried out, Mw (weight average molecular weight) was 9700, and degree of dispersion (Mw/Mn) was 2.31.

[0070] Composition of the resin of the example 14 following structure [** 26]



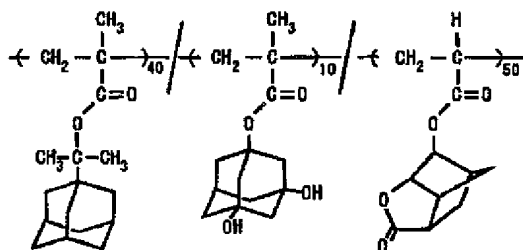
In an example 11 as a monomer component (A)1-(1-methacryloyloxy-1-methylethyl) adamantane (IAM) 35.62g, (B) 1-acryloyloxy -3 and 5-dihydroxy adamantane (DHAA) 8.09g, (C) 1-methacryloyloxy-3-hydroxy adamantane (HMA) 8.02g, (D) -- except having used 5-acryloyloxy -2 and 6-norbornane KARUBO lactone (ANBL) 28.28g (a monomer presentation ratio -- (A):(B):(C):(D) =40:10:10:40) When reacted by the same actuation as an example 11, 73g of desired resin was obtained. When GPC analysis of the collected polymer was carried out, Mw (weight average molecular weight) was 13400, and degree of dispersion (Mw/Mn) was 3.15.

[0071] Composition of the resin of the example 15 following structure [** 27]



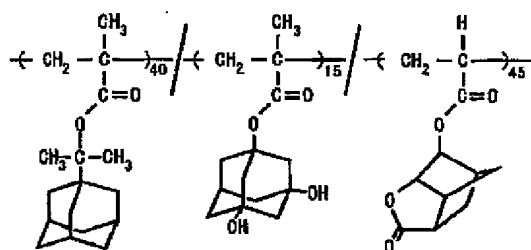
In an example 11 as a monomer component (A)1-(1-methacryloyloxy-1-methylethyl) adamantane (IAM) 43.78g, (B) 1-methacryloyloxy - 3, 5-dihydroxy adamantane (DHMA) 8.42g, (C) -- except having used 5-acryloyloxy -2 and 6-norbornane KARUBO lactone (ANBL) 27.80g (a monomer presentation ratio -- (A):(B):(C) =50:10:40), when reacted by the same actuation as an example 11, 71g of desired resin was obtained. When GPC analysis of the collected polymer was carried out, Mw (weight average molecular weight) was 15600, and degree of dispersion (Mw/Mn) was 3.27.

[0072] Composition of the resin of the example 16 following structure [** 28]



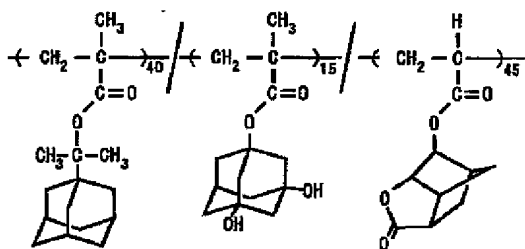
in the example 15, except having used (A)35.83g, (B)8.62g, and (C)35.56g (a monomer presentation ratio -- (A):(B):(C) =40:10:50) as a monomer component, when reacted by the same actuation as an example 15, 72g of desired resin was obtained. When GPC analysis of the collected polymer was carried out, Mw (weight average molecular weight) was 12700, and degree of dispersion (Mw/Mn) was 2.67.

[0073] Composition of the resin of the example 17 following structure [** 29]



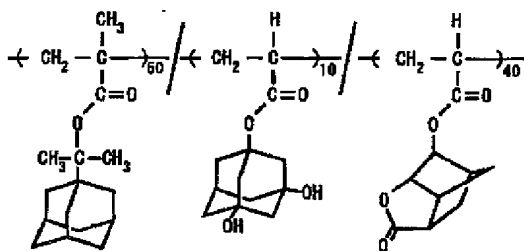
In an example 13 as a monomer component (A)1-(1-methacryloyloxy-1-methylethyl) adamantane (IAM) 35.50g, (B) 1-methacryloyloxy - 3, 5-dihydroxy adamantane (DHMA) 12.80g, (C) -- except having used 5-acryloyloxy -2 and 6-norbornane KARUBO lactone (ANBL) 31.70g (a monomer presentation ratio -- (A):(B):(C) =40:15:45), when reacted by the same actuation as an example 13, 74g of desired resin was obtained. When GPC analysis of the collected polymer was carried out, Mw (weight average molecular weight) was 10000, and degree of dispersion (Mw/Mn) was 2.52.

[0074] Composition of the resin of the example 18 following structure [** 30]



In the example 17, except having used ethyl lactate instead of propylene glycol monomethyl ether, when reacted by the same actuation as an example 17, 70g of desired resin was obtained. When GPC analysis of the collected polymer was carried out, Mw (weight average molecular weight) was 6500, and degree of dispersion (Mw/Mn) was 2.10.

[0075] Composition of the resin of the example 19 following structure [** 31]



In an example 11 as a monomer component (A)1-(1-methacryloyloxy-1-methylethyl) adamantane (IAM) 44.03g, (B) 1-acryloyloxy -3 and 5-dihydroxy adamantane (DHAA) 8.00g, (C) -- except having used 5-acryloyloxy -2 and 6-norbornane KARUBO lactone (ANBL) 27.97g (a monomer presentation ratio -- (A):(B):(C) =50:10:40), when reacted by the same actuation as an example 11, 69g of desired resin was obtained. When GPC analysis of the collected polymer was carried out, Mw (weight average molecular weight) was 11500, and degree of dispersion (Mw/Mn) was 2.47.

[0076] In example of comparison 1 example 1, instead of PGMEA, when reacted by the same actuation as an example 1, 54g of desired resin was obtained to the polymerization solvent except having used the tetrahydrofuran (THF). When GPC analysis of the collected polymer was carried out, Mw (weight average molecular weight) was 7240, and degree of dispersion (Mw/Mn) was 2.30.

[0077] In example of comparison 2 example 2, instead of PGMEA, when reacted by the same actuation as an example 2, 58g of desired resin was obtained to the polymerization solvent except having used THF. When GPC analysis of the collected polymer was carried out, Mw (weight average molecular weight) was 10400, and degree of dispersion (Mw/Mn) was 2.20.

[0078] In example of comparison 3 example 3, instead of PGMEA, when reacted by the same actuation as an example 3, 61g of desired resin was obtained to the polymerization solvent except having used THF. When GPC analysis of the collected polymer was carried out, Mw (weight average molecular weight) was 11000, and degree of dispersion (Mw/Mn) was 1.90.

[0079] In example of comparison 4 example 4, instead of PGMEA, when reacted by the same actuation as an example 4, 55g of desired resin was obtained to the polymerization solvent except having used THF. When GPC analysis of the collected polymer was carried out, Mw (weight average molecular weight) was 9300, and degree of dispersion (Mw/Mn) was 2.33.

[0080] In example of comparison 5 example 12, instead of PGMEA, when reacted by the same actuation as an example 12, 76g of desired resin was obtained to the polymerization solvent except having used 1,4-dioxane. When GPC analysis of the collected polymer was carried out, Mw (weight average molecular weight) was 10600, and degree of dispersion (Mw/Mn) was 2.69.

[0081] In example of comparison 6 example 17, instead of the mixed solvent of PGMEA and PGME, when reacted by the same actuation as an example 17, 75g of desired resin was obtained to the polymerization solvent except having used 1,4-dioxane. When GPC analysis of the collected polymer was carried out, Mw (weight average molecular weight) was 9600, and degree of dispersion (Mw/Mn) was 2.37.

[0082]

[A table 1]

表 1

		モノマー [モル%]									溶媒
		ANBL	MNBL	HMA	HAA	DHMA	DHAA	IAM	IAA	2MMA	
実施例	1		25	30						45	PGMEA
	2		25		25					50	PGMEA
	3	25		25				50			PGMEA
	4	30		30				40			PGMEA
	5	40		20				40			PGMEA
	6	20		40				40			PGMEA
	7	40		30				30			PGMEA
	8	30		40				30			PGMEA
	9		30	30					40		PGMEA
	10	25			25				50		PGMEA
	11	30		10		10		50			PGMEA
	12	40		10		10		40			PGMEA
	13	20		20		10		50			PGMEA/PGME
	14	40		10			10	40			PGMEA
	15	40				10		50			PGMEA
	16	50				10		40			PGMEA
	17	45				15		40			PGMEA/PGME
	18	45				15		40			PGMEA/EL
	19	40					10	50			PGMEA
比較例	1		25	30						45	THF
	2		25		25					50	THF
	3	25		25				50			THF
	4	30		30				40			THF
	5	40		10		10		40			Dioxane
	6	45				15		40			Dioxane

[0083] About the polymer obtained from the assessment test (solvent solubility) above-mentioned example and the example of a comparison, the polymer 100 weight section and the triphenylsulfonium hexafluoroantimonate 10 weight section were mixed to the solvent, and the solubility when preparing the resin constituent for photoresists of 17 % of the weight of polymer concentration was investigated. About the polymer obtained from the examples 1-6 of a comparison in the solvent same about the polymer obtained from examples 1-19 as a solvent as each polymerization solvent, propylene-glycol-monomethyl-ether acetate (PGMEA) was used, and the mixed solvent (weight ratio 8:2) of PGMEA and propylene glycol monomethyl ether (PGME) was used about the polymer obtained from the example 7 of a comparison. When it dissolved easily to these solvents, it did not dissolve in O and a solvent when it becomes a transparent solution, but nebula and precipitate were seen, it evaluated as x. These results are shown in a table 2.

[0084] (Resist engine performance) The same solvent as each polymerization solvent was mixed [the polymer obtained from the above-mentioned example] for the polymer 100 weight section and the triphenylsulfonium hexafluoroantimonate 10 weight section as a solvent, and the resin constituent for photoresists of 17 % of the weight of polymer concentration was prepared. The obtained constituent was applied with the spin coating method on the silicon wafer, and the sensitization layer with a thickness of 1.0 micrometers was formed. After prebaking for 150 seconds at the temperature of 100 degrees C with a hot plate, the KrF excimer laser with a wavelength of 247 micrometers was exposed by dose 30 mJ/cm² through the mask which has 0.2-micrometer line - and - tooth-space pattern. After carrying out postbake for 60 seconds at the temperature of 100 degrees C with a hot plate, negatives were developed for 60 seconds using the 0.3M tetramethylammonium hydroxide water solution, and the rinse was carried out with pure

water. That from which the turbulence of O and a pattern etc. produced that from which 0.2-micrometer line – and – tooth-space pattern were obtained on the silicon wafer was evaluated as x. These results are shown in a table 2.

[0085]

[A table 2]

表 2							
		Mw	Mw/Mn	収量 [g]	溶剤溶解性		レジスト 性能
					溶剤	溶解性	
実施例	1	6,800	2.10	56	PGMEA	○	○
	2	13,400	2.40	60	PGMEA	○	○
	3	11,400	1.91	63	PGMEA	○	○
	4	8,300	2.03	58	PGMEA	○	○
	5	8,600	2.10	59	PGMEA	○	○
	6	9,100	2.15	58	PGMEA	○	○
	7	15,100	3.70	60	PGMEA	○	○
	8	14,400	2.03	62	PGMEA	○	○
	9	6,800	1.94	58	PGMEA	○	○
	10	7,000	2.11	54	PGMEA	○	○
	11	14,900	3.17	69	PGMEA	○	○
	12	13,200	2.98	72	PGMEA	○	○
	13	9,700	2.31	65	PGMEA/PGME	○	○
	14	13,400	3.15	73	PGMEA	○	○
	15	15,600	3.27	71	PGMEA	○	○
	16	12,700	2.67	72	PGMEA	○	○
	17	10,000	2.52	74	PGMEA/PGME	○	○
	18	6,500	2.10	70	PGMEA/EL	○	○
	19	11,500	2.47	69	PGMEA	○	○
比較例	1	7,240	2.30	54	PGMEA	×	—
	2	10,400	2.20	58	PGMEA	×	—
	3	11,000	1.90	61	PGMEA	×	—
	4	9,300	2.33	55	PGMEA	×	—
	5	10,600	2.69	76	PGMEA	×	—
	6	9,600	2.37	75	PGMEA/PGME	×	—

It dissolved easily to each solvent and the polymer obtained from examples 1-19 became a transparent solution. On the other hand, the polymer obtained from the examples 1-7 of a comparison was not dissolved in the above-mentioned solvent, but nebula or precipitate was seen. The resin constituent for resists prepared from the polymer furthermore obtained according to examples 1-19 demonstrated the high resist engine performance also to the detailed pattern.

[Translation done.]